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Simple and accurate quantification of BTEX in ambient air by SPME and GC–MS

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Abstract
Benzene, toluene, ethylbenzene and xylenes (BTEX) comprise one of the most ubiquitous and hazardous groups of ambient air pollutants of concern. Application of standard analytical methods for quantification of BTEX is limited by the complexity of sampling and sample preparation equipment, and budget requirements. Methods based on SPME represent simpler alternative, but still require complex calibration procedures. The objective of this research was to develop a simpler, low-budget, and accurate method for quantification of BTEX in ambient air based on SPME and GC–MS. Standard 20-mL headspace vials were used for field air sampling and calibration. To avoid challenges with obtaining and working with 'zero' air, slope factors of external standard calibration were determined using standard addition and inherently polluted lab air. For polydimethylsiloxane (PDMS) fiber, differences between the slope factors of calibration plots obtained using lab and outdoor air were below 14%. PDMS fiber provided higher precision during calibration while the use of Carboxen/PDMS fiber resulted in lower detection limits for benzene and toluene. To provide sufficient accuracy, the use of 20 mL vials requires triplicate sampling and analysis. The method was successfully applied for analysis of 108 ambient air samples from Almaty, Kazakhstan. Average concentrations of benzene, toluene, ethylbenzene and o-xylene were 53, 57, 11 and 14 μg m−3, respectively. The developed method can be modified for further quantification of a wider range of volatile organic compounds in air. In addition, the new method is amenable to automation.

Keywords
Solid-phase microextraction, GC–MS, Standard addition, BTEXAmbient air pollution, Air analysis

Disciplines
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Comments
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Measurement of benzene, toluene, ethylbenzene and *o*-xylene concentrations in ambient air of Almaty, Kazakhstan, by solid-phase microextraction and gas chromatography - mass spectrometry

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Abstract

Kazakhstan is experiencing unprecedented growth in large urban areas with unintentional, negative impact on air quality. Benzene, toluene, ethylbenzene and xylenes (BTEX) are one of the most ubiquitous and hazardous ambient air pollutants of concern. There is no published information on BTEX concentrations in ambient air of Almaty, the largest city of Kazakhstan, mainly due to a complexity and budget limitations of standard air sampling and analytical procedures. The objective of this research was to develop a simple, vial-based method for whole air sample collection, and then measure BTEX concentrations in ambient air of Almaty. Gas samples were prepared using solid-phase microextraction (SPME) and analyzed with gas chromatography–mass spectrometry. Air sampling method was optimized for simplicity, improved stability, and recovery of BTEX concentrations in samples. Air samples were collected at six locations in different areas of Almaty on March 31, April 2 and 4, 2015 at 8 A.M. and 8 P.M. Mean concentrations of BTEX analytes at different sampling times ranged from 24 to 89, from 32 to 96, from 6 to 23 and from 7 to 32 μg/m^3, respectively. Mean (of all analyzed 108 samples) BTEX concentrations were 53, 57, 11 and 14 μg/m^3, respectively. BTEX concentrations decreased with the increased elevation. Highest concentrations were measured on the coldest day when most BTEX originated from residential heating. Obtained results suggest that ambient air in Almaty should be of much greater concern. Measured BTEX concentrations were comparable with those in the most polluted large cities around the world.

Keywords

BTEX; air pollution; monitoring; Almaty; solid-phase microextraction; GC-MS.

1. Introduction

Rapid population growth, urban sprawl, increased energy usage and transportation cause serious air pollution in many cities around the world (Lan and Minh, 2013). Air pollution causes disruption of ecosystems and creates economic and social cost. It can lead to significant risks to human health at both local and regional scales all over the world. According to the World Health Organization (WHO), outdoor air pollution was responsible for the death of 3.7 million people under the age of 60 in 2012, 90% of whom lived in developing countries (WHO, 2014). The WHO air quality database continuously increases and covers today 1,600 cities in 91 countries (WHO, 2014) demonstrating significant problems with urban air quality.

One of the most hazardous groups of air pollutants are volatile organic compounds (VOCs) (Caselli et al., 2010; EPA, 2010; Wark and Warner, 1977). Within VOCs, special attention is paid to benzene, toluene, ethylbenzene and *o*-, *p*-and *m*-xylenes (BTEX). BTEX are emitted to the atmosphere from both anthropogenic and biogenic sources (Alghamdi and Khoder, 2014), and can further be formed photochemically (Atkinson and Arey, 2003). In larger cities, the main sources of BTEX are the transportation, power plants, industrial enterprises, and construction works (Gelencsér et al., 1994; Helmig and Thompson, 2014; Lerner and Kohajda, 2014).

Major BTEX exposure routes for humans are either through the respiratory system or through skin contact or through (Li and Li, 2014). These compounds can also pose a serious threat to human health through interaction with chemical compounds present in the body (Table A1 in SM). Benzene is known as a Group 1 carcinogen to human's health (Caselli et al., 2010; Kerbachia et al., 2006). Benzene's cancer risk evaluation guide (CREG), defined as target risk level/inhalation unit risk ratio at 0.03 ppb (0.1 $\mu g/m^3$) (Letter Health Consulation, 2015) the regional screening level (RSL) being 0.1 ppb (Atlantic Risk Assessment, 2012). An oral cancer slope factor for benzene (CSF) derived from an extrapolation from inhalation dose-response data ranges from 1.5×10^{-2} to 5.5×10^{-2} $(mg/kg/d)^{-1}$ (EPA, 2009).

Many counties regulate and mandate monitoring BTEX concentrations in ambient air. Thus, the U.S. EPA has established a reference concentration (RfC) of 30 $\mu g/m^3$ for benzene in air based on hematological effects in humans (EPA, 2009). In the European Union, average annual concentration of benzene is limited to 5 $\mu g/m^3$ (European Commission, 2010). In Kazakhstan, maximum allowable concentrations (MAC) of benzene for a single and 24-h average

measurements are 300 and 100 μg/m^3, respectively (Russian Ministry of Health, 2003) – 20-60 times the limit within the European Union.

According to previously reported studies, BTEX are found in highest concentrations in a typical ambient large city air among all other VOCs. Reported concentrations of BTEX in ambient city air varied from 0.8 to 87, 3 to 268, 0.9 to 167 and 0.3 to 38 μg/m^3, respectively for the four BTEX compounds (Table 1).

Table 1 – Ambient air BTEX concentrations in selected cities in the world

Country	City	Concentration, μg/m^3					Reference
		Benzene	Toluene	Ethylbenzene	Xylene		
					m+p	*o*	
Africa							
Egypt	Cairo[e]	67	16-23	3	9-12	3-4	(Khoder, 2007)
America							
Brazil	Porto Alegre[e]	22	37	20	36	-	(Grosjean, 1998)
	Sao Paulo[e]	10-17	18-28	3-6	10-19	4-6	(Gee and Sollars, 1998)
Canada	Windsor[e]	0.8	3	0.5	1	0.5	(Miller and Xu, 2012)
Chile	Santiago[e]	11-15	14-30	3-7	15-25	6-9	(Gee and Sollars, 1998)
Asia							
China	Beijing[d]	2-3	6-9	2-3	3-5	2	(Zhang and Mu, 2012)
	Beijing[a]	2	4	2	4	2	(Liu and Mu, 2009)
	Hong Kong[e]	3-15	5-139	2-25	3-28	1-13	(Lee and Chiu, 2002)
India	New Delhi[e]	87	167	17	67	35	(Hoque and Khillare, 2008)
Japan	Tokyo[e]	3-7	-	-	-	-	(Laowagul and Yoshizumi, 2009)
	Yokohama[e]	7	20	13	9	3	(Tiwari et al., 2010)
Kazakhstan	Almaty[b]	53	57	11	-	14	This study
Nepal	Kathmandu[e]	2-13	-	-	-	-	(Gautam, 2004)
Philippines	Manila[b]	12	84	-	-	38	(Balanay and Lungu, 2009)
Taiwan	Kaohsiung[e]	7-25	9-57	2-11	10-23	4-9	(Hsieh and Yang, 2006)
Thailand	Bangkok[a]	15-42	-	-	-	-	(Leong et al., 2002)
Turkey	Eskişehir[a]	1	6	0.3	0.5	0.4	(Demirel and Ozden, 2014)
	Kocaeli[c]	2	36	10	37	13	(Pekey and Yılmaz, 2011)
Vietnam	Ho Chi Minh[a]	56	121	21	64	23	(Huong and Nguyen, 2014)
Australia							
New Zealand	Christchurch[e]	1-9	2-27	0.6-4	1-23		(Mccauley, 2005)
Europe							
United Kingdom		Up to 6.3	-	-	-	-	(DEFRA UK, 2012)
Belgium	Mortsel[b]	0.6-6	3-16	0.3-3	1-6	0.3-3	(Buczynska and Krata, 2009)
Italy	Bari[b]	0.8-9	0.9-16	0.2-3	0.8-10	0.3-4	(Caselli et al., 2010)
	Rome[e]	40-47	128-138	-	-	-	(Brocco and Fratarcangeli, 1997)

Note:
[a] – 24-h average concentration
[b] – 1-week average concentration
[c] – Monthly average concentration
[d] – Seasonally averaged concentration
[e] – Annual average concentration
-- Not reported

Almaty is the largest city in Kazakhstan with the increasing population of approx. 1.5 million. Almaty is considered as one of the most attractive places in Kazakhstan to live. However, the unintended consequence of the economic growth is that the air pollution in Almaty over the past 15 y has reached levels comparable with the most polluted cities in the world (Kazakhstan Today, 2008). The reasons are complex, but the main factors are geography, increasing number of vehicles, infrastructure not adequate to fully accommodate growth, and fuel quality. Today more than 500 thousand registered cars in Almaty of which 60% are at least than 10 y old, some of which have outdated emissions control technology (Kadyrbaev, 2015; Seidakhmetova, 2014). The geographical location of the city exacerbates air pollution. Almaty is surrounded by the Trans-Ili Mountains and located in valleys of the Big and Small Almatinka Rivers. Mountains and hills limit the horizontal movement and exchange of air. Cold air from mountains often causes temperature inversions and poor vertical air movement. In addition, Almaty ranks as #1 (out of 17 cities/provinces) in Kazakhstan on respiratory, endocrine and blood diseases, cancer and bronchial asthma per capita (Konurkulzhaeva, 2014).

According to a recent screening of the air quality with solid phase microextraction (SPME) and gas chromatography – mass spectrometry (GC-MS) (Carlsen et al., 2013), more than 100 VOCs were identified in Almaty ambient air, with BTEX being the most abundant. However, to date, there is no actual data on concentrations of BTEX in the ambient air of Almaty, mainly due to budget limitations and complexity of standard analytical methods. The objective of the present study is to remedy this.

Current standard approaches for quantification of BTEX (EPA, 1999; Feng and Mitra, 2000; Quality Assurance Team, 2004) are mainly based on trapping analytes into evacuated canisters or onto sorbent tubes followed by thermal desorption, cryogenic focusing and GC-MS. Despite of good reliability, these techniques are quite complex, labor-, time-consuming, and require additional sampling and sample preparation equipment. Additional problems may include carryover of analytes and clogging of the cryogenic focusing system, which considerably limit the application of standard methods, not least in developed countries.

To remedy these problems solid-phase microextraction (SPME) (Elke and Jermann, 1998; Khaled and Pawliszyn, 2000; Martos and Pawliszyn, 1999, Augusto et al., 2001) constitutes an attractive alternative method for screening and quantification of VOCs in air. The SPME technology combines sampling and sample preparation. SPME is based on passive extraction of VOCs by a thin polymer coating followed by desorption of analytes in GC injection port. The use of SPME does not require thermal desorption unit. Desorption of VOCs from SPME is rapid, and it does not require cryogenic focusing. SPME fiber cleanup is done in GC injection port and is not required after the analysis of a previous sample, i.e., SPME fibers can be reused for gas sampling.

SPME is widely used for determination range of VOCs in ambient air (Chai and Tang, 1998; Elke and Jermann, 1998; Haberhauer-Troyer et al., 1999; Italiana and Tumbiolo, 2005; Koziel and Jia, 1999; Koziel and Pawliszyn, 2001; Prikryl and Sevcik, 2008; Tuduri et al., 2002; Tumbiolo and Gal, 2004; Yassaa et al., 1999). Researchers (Xiong et al., 2004) reported on BTEX sampling with SPME in the presence of ozone. (Table A2 in Supplementary Material, SM). Review of SPME applications for indoor air is presented elsewhere (Koziel and Novak, 2002). Most recently, SPME has also been used to quantify BTEX concentrations in vehicle exhausts (Baimatova et al., 2015) and hot industrial gas streams (Woolcock and Koziel, 2013, 2015). Despite the high efficiency of SPME for determination of VOCs in air (Table A2 in SM), there are still challenges limiting its application and its standardization. The most crucial problem is the insufficient accuracy of the method for determination of VOCs in air. Specifically:

- competition between analytes due to a low sorbent capacity of the fiber;
- uncontrolled adsorption of analytes on metal parts of fiber holder;
- effects of turbulence and diffusion boundary layer (around the SPME) on the rate of sampling with exposed SPME fibers;
- effects of air temperature on SPME extraction efficiency.

Some authors report problems with labor-intensive calibration, i.e., requirement to construction of a system for generation of air with known concentration of the analyte (Haberhauer-Troyer et al., 1999; Tumbiolo and Gal, 2004). However, many of these challenges can be addressed with (e.g.) retracted SPME fiber approach (Woolcock et al., 2015; Baimatova et al., 2015).

The objective of this research was to develop a simple method for sample collection and analysis and then measure BTEX concentrations in ambient air of Almaty applying SPME-GC-MS. Air sampling was optimized for higher simplicity, recovery, and stability of BTEX concentrations.

2. Experimental

2.1 *Air sampling sites*

Samples were collected at six sites located in five different districts (Bostandyk, Auezov, Medeu, Almaly and Turksib) of Almaty city, Kazakhstan (Fig. 1). Sites S1-S6 were chosen in different parts of the city for assessment of average and representative pattern of BTEX in the whole city. Sites S1-S6 are located near the main streets of the city – al-Farabi Ave., Abay Ave., Sain Str., Suyunbay Ave. Samples were taken at the height 1.5-1.8 m above the ground, which where the major inhalation by pedestrians takes place. Sampling was taken at the distance >15 m

from the road. Meteorological parameters such as temperature, wind speed and humidity of the air were obtained from publically-available data base (Kazhydromet, 2015).

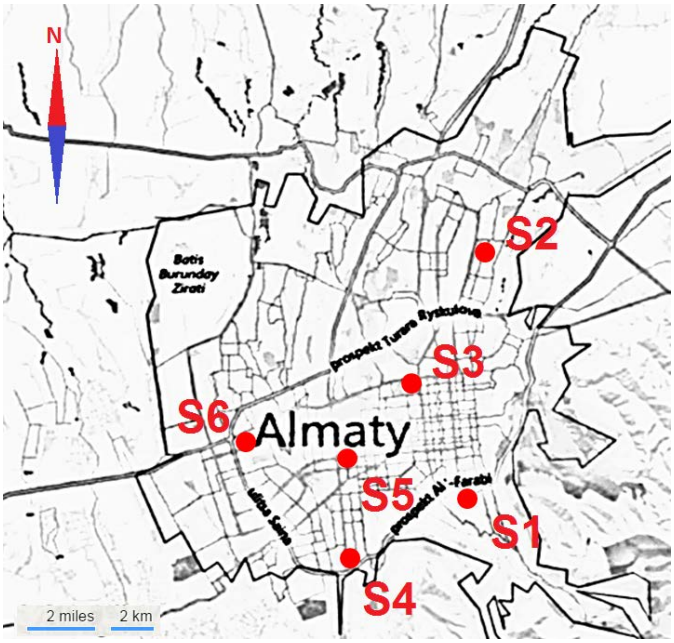

Figure 1 – Location of sampling sites S1-S6

Air sampling was done on March 31, April 2 and 4, 2015. Sampling at each location was carried out at 8 A.M. and 8 P.M using 'crowd-sourcing', i.e., trained students from our research group. Air samples were collected into 20 mL vials in triplicates. Thirty six samples were taken each day; the total number of analyzed samples was 108. Vials were packed into 1 L clean glass jars, sealed and transported to the laboratory (Fig. A1 in SM). Sample vials were removed from jars immediately before the analysis to minimize interferences to BTEX concentrations. All air samples were analyzed within 4 h after collection. Measured BTEX concentrations were not adjusted for temperature and pressure changes between sampling sites (Table 2) and analysis, which contribute uncertainties to concentration measurement.

Table 2 – Weather conditions on sampling days

Date	Air temperature, °C		Condition	Wind speed, m/s	Pressure, mm	Humidity, %
	8 A.M.	8 P.M.				
3/31/2015	-10	-4	sunny	1	691	60
4/2/2015	-4	0	snowing	3	689	77
4/4/2015	+4	+11	sunny	0	690	60

2.2 Air sampling by SPME

Ambient air samples were collected into 20 mL crimp-top vials (i.e., by opening vial to air and shaking of ~60 sec to increase air exchange) and then sealed with aluminum caps equipped

with PTFE-Silicone septa (Agilent, USA). Crimp-top vials were chosen over screw top vials to minimize analyte losses based on preliminary experiments. Prior to sampling, all vials and septa were washed by a distilled water and pre-conditioned at 160 °C for 4 h. Vials with air samples were placed into the Combi-PAL (CTC Analytics AG, Switzerland) agitator for further analysis by GC-MS. Air samples were passively extracted from vial using exposed 100 µm polydimethylsiloxane (100 µm PDMS) SPME fiber (Supelco, Bellefonte, PA, USA). 100 µm PDMS fiber is not the most selective fiber for BTEX (Elke and Jermann, 1998; Paschke and Vrana, 2006; Popp and Paschke, 1997). However, the use of PDMS was associated with improved data reproducibility in this research. This was likely due to a higher volume of PDMS fiber coating and less pronounced competition between analytes (Pawliszyn, 2012). Extraction was done at a constant temperature of 30 °C for 3 min, pre-incubation time was set to 3 min. The optimal extraction time was chosen experimentally as equilibration time between SPME coating and vial headspace (Figure A2 in SM).

2.3 *Air sample analyses with GC-MS*

All gas samples were analyzed on 7890A/5975C Triple-Axis Detector diffusion pump based (Agilent, Santa Clara, USA) GC-MS equipped with split/splitless inlet. For separation of BTEX, a 30 m × 0.25 mm HP-INNOWax (Agilent, USA) column with film thickness 0.25 µm was used. The constant flow of He in column was 1 mL/min. Temperatures of ion source, quadrupole and MS interface were 230, 150 and 250 °C, respectively. Thermal desorption of analytes from SPME fiber in GC injector was done in splitless mode at 250 °C using 0.75 mm i.d. liner (Supelco, USA). Oven temperature was programmed from initial 40 °C (held for 3 min) to 150 °C (held for 1.5 min) at the heating rate of 20 °C/min. GC column retention times for BTEX were 3.5, 4.9, 5.8 and 6.4 min, respectively. Detection was carried out in selected ion monitoring (SIM) mode at m/z 78, 91, 106 and 106 for selective detection and quantification of the four BTEX constituents, respectively. Total GC run time of the analysis was 10 min.

2.4 Calibration and quantitative determination of BTEX

Benzene (99.8%) and toluene (99.8%) were obtained from EKOS-1 LLP (Moscow, Russia). Ethylbenzene (99.0%), and *o*-xylene (99.0% purity) were purchased from Sigma-Aldrich, St. Louis, MO, USA. Methanol (HPLC grade) was obtained from AppliChem (Darmstadt, Germany). Helium (>99.995%) was purchased from “Orenburg-Tehgas” (Orenburg, Russia).

Presence of BTEX in the air is a common challenge for many air quality laboratories where special air handling and conditioning is not feasible. Due to the presence of BTEX in the indoor air of the lab, calibration plots were obtained by a standard addition method. To prepare calibration

samples, open 20-mL vials were left on a laboratory table for 15 min followed by an injection of 1 µL aliquots of liquid BTEX standard solutions and sealing with crimped tops. The advantage of such methodology is that it does not necessarily require knowing real concentrations of analytes in calibration samples because the obtained calibration slope should be equal to the slope for external standard calibration. The proposed approach substantially simplified the calibration process because "zero" air was not required for the calibration. Filling vials with "zero" air would also be complicated. Calibration for benzene and toluene was done separately from ethylbenzene and *o*-xylene because of different target concentration ranges (Table 3). Detailed description of a strategy for preparation of calibration samples is provided in SM.

Obtained SIM mode chromatograms were integrated for peak area counts. BTEX compounds were identified using retention times of single analytes and spectral matches. Obtained calibration plots for BTEX were linear in the whole studied standard addition concentrations range 20-200 µg/m^3 for benzene and toluene and 2-20 µg/m^3 for ethylbenzene and *o*-xylene (Fig. A3 in SM) with the squared correlation coefficients R^2>0.99 (Table 3). Mean relative standard deviations ranged from 1 to 5%. According to the calibration, BTEX concentrations in lab air are 63, 44, 2 and 3 µg/m^3, respectively.

Table 3 – Results of GC-MS calibration by SPME fiber

Analyte	GC Column Retention time, min	Concentration range, µg/m^3	R^2	Intercept, kAU	Slope, (kAU m^3)/µg	C in lab air, µg/m^3
Benzene	3.5	20-200	0.9937	35±4	0.55±0.03	63
Toluene	4.9	20-200	0.9946	60±1	1.40±0.08	44
Ethylbenzene	5.8	2-20	0.9927	5.0±2.0	2.9±0.2	2
o-Xylene	6.4	2-20	0.9934	23±5	8.1±0.5	3

Note: kAU - Kilo Arbitrary Units

2.5 Optimization of air sampling procedure

Optimization of air sampling consisted of:

2.5.1 Comparison of the mass extracted by SPME from 250 mL bulbs and from 20 mL vials.

Prior to sampling, vials and bulbs (Sigma-Aldrich, St. Louis, MO, USA) were washed by distilled water and pre-conditioned at 160 °C during 4 h. Ambient air samples were collected in bulb by pumping at flow rate 1 L/min during 5 min and into 20 mL crimp-top vials (i.e., by opening vial to air and shaking of ~60 sec to increase air exchange) and then sealed with aluminum caps with PTFE-Silicone septa (Agilent, USA). All samples were analyzed in triplicates by SPME-GC-MS using the method as for analyses of gas samples in vials.

The objective of this experiment was to compare BTEX mass extracted by SPME from the same air located in 250 mL calibrated bulb and from 20 mL vial. Masses extracted from the bulb

were 3%, 17%, 18% and 9% higher than those from vial for BTEX, respectively (Table 4). The difference is in the range of standard deviation (Table 4) meaning that BTEX can be extracted from 20 mL vial without a significant loss of recovery.

Table 4 – Comparison of BTEX mass extracted from air samples collected with glass bulbs and vials

Compound	Mass extracted by SPME, pg	
	250 mL bulb	20 mL vial
Benzene	2.7±0.2	2.7±0.6
Toluene	2.3±0.6	1.9±0.1
Ethylbenzene	0.88±0.08	0.7±0.1
o-Xylene	1.30±0.03	1.2±0.1

2.5.1 Study of a stability of BTEX concentrations inside vials

BTEX concentration in air inside vials may change due to a difference of their concentrations in a sampled and outside (e.g., lab) air. Stability of BTEX concentrations inside vials during their transportation and storage was checked by analysis of BTEX concentrations in vials filled with 'clean' air at different time periods - 1, 5 and 12 day after sampling. 'Clean' air was collected in mountains at a distance of 15 km from Almaty and a height of 2700 m in relatively non-polluted area (N43^{0}3.303'; E76^{0}58.563').

BTEX concentrations in 'clean' air samples were less than 12% of those in the ambient air for up to 12 d of a sample storage in vials using the proposed sampling approach. Such results indicate the effectiveness of the proposed approach and very good stability of BTEX concentrations inside vials (Fig. A4 in SM). This result is important because it shows that small leaks via septa and a concentration gradient between sampled and ambient air are negligible. Problems with sample stability associated with air sampling can be sometimes detrimental as analyte concentrations inside sample bags and containers may vary during storage and transportation and cause problems with accuracy of the results.

3. RESULTS AND DISCUSSIONS

3.1 *Quantification of BTEX concentrations in ambient air of Almaty*

Developed method was applied to air samples in Almaty city. Examples of the analyzed air are presented in Fig. 2. Chromatograms of air samples had a high resolution of the relevant peaks (Fig. 2), signal to noise ratio being greater than 15:1 for all analytes in the studied samples. Mean concentrations (for all 18 air samples per all six locations) of benzene, toluene, ethylbenzene and *o*-xylene at different sampling periods ranged from 24 to 89, 32 to 96, 6 to 23 and 7 to 32

μg/m^3, respectively. Average concentrations of BTEX compounds calculated as a mean of all 108 measurements were 53, 57, 11 and 14 μg/m^3, respectively.

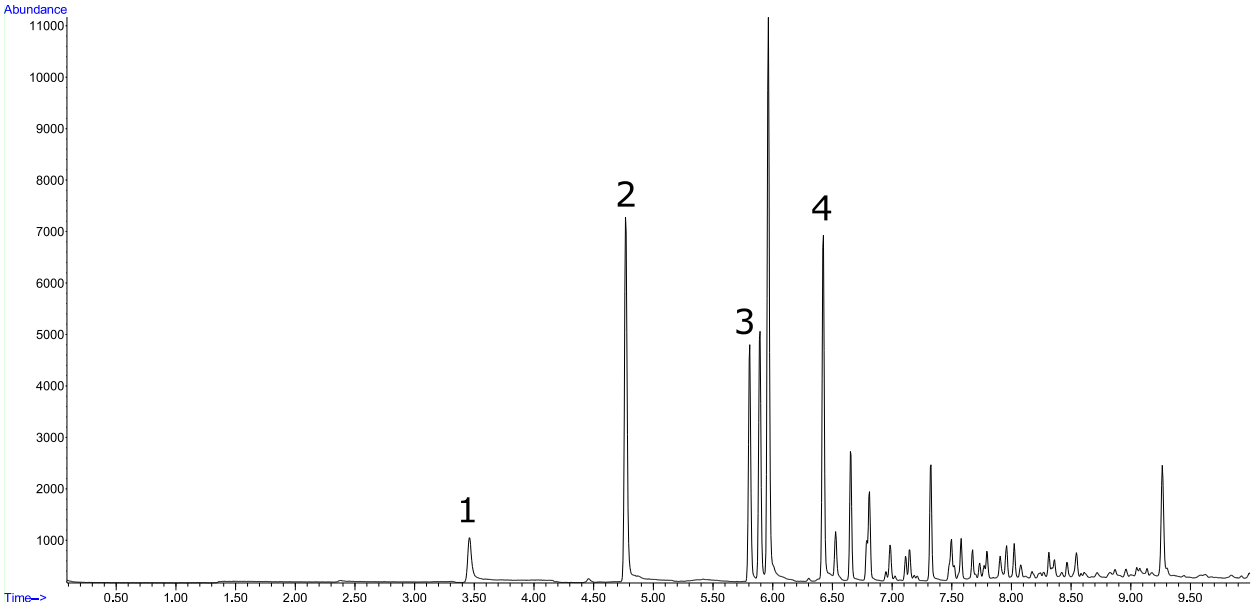

Figure 2 – Chromatogram of air sample collected at site S3 at 8 P.M. on April 2, 2015.
Note: 1 – benzene (36 μg/m^3), 2 – toluene (67 μg/m^3), 3 – ethylbenzene (12 μg/m^3), 4 – o-xylene (18 μg/m^3)

Table 5 – Mean concentrations of BTEX in air at different time periods and locations of Almaty city

		Concentration ± Standard Deviation, μg/m^3									
Time of sampling >		8:00 A.M.			8:00 P.M.			Daily			All
Date of sampling >		March 31	April 2	April 4	March 31	April 2	April 4	March 31	April 2	April 4	
Benzene	Mean	85±23	89±73	26±10	63±17	33±10	24±3	74±23	61±58	25±7	53±41
	Max	122	237	37	88	51	27	122	237	43	237
	Min	58	46	17	43	21	20	43	23	17	17
Toluene	Mean	43±22	96±195	46±30	59±41	62±32	32±13	51±33	79±134	39±23	56±80
	Max	82	494	98	133	100	55	133	494	98	494
	Min	26	10	24	18	22	19	18	10	19	10
Ethylbenzene	Mean	8±3	23±42	10±8	13±8	10±4	6±1	10±7	16±30	7±4	11±17
	Max	13	108	20	27	17	7	27	107	20	107
	Min	6	4	5	4	4	5	4	4	5	4
o-Xylene	Mean	9±4	32±66	10±8	15±10	13±7	7±2	12±8	22±46	8±6	14±27
	Max	15	166	24	31	22	9	31	166	24	166
	Min	6	3	5	3	4	4	3	3	4	3

Concentrations of ethylbenzene and *o*-xylene were approx. one order of magnitude less than those of benzene and toluene (Table 5), which may be explained by their lower stability in air (Prinn et al., 1987), concentrations in a gasoline (Carlsen et al., 2013) and exhaust gases of cars (Baimatova et al., 2015). Similar relationship between BTEX concentrations was also reported in earlier studies (Baimatova et al., 2015) .

Relative standard deviations of triplicate ambient air measurements did not exceed 25% with most replicates being in the range of 10%, which is excellent and sufficient considering the simplicity of the approach for sampling of ambient air. Over the whole study, only twelve misses were found (<11% of total samples), likely caused by a damage of vial crimps and subsequent leakage.

BTEX concentrations in air in five studied districts of Almaty (Medeu, Turksib, Almaly, Auezov, Bostandyk) were different from each other (Fig. 3). The lowest concentrations of BTEX were found in Bostandyk district, the largest - in Turksib district. Bostandyk district is situated in upper (south) part of city, closer to mountains, where circulation of mountain-valley air is likely. Turksib district is situated at the lower altitude, close to the city center, which is typically overloaded with traffic jams and has a poor air circulation.

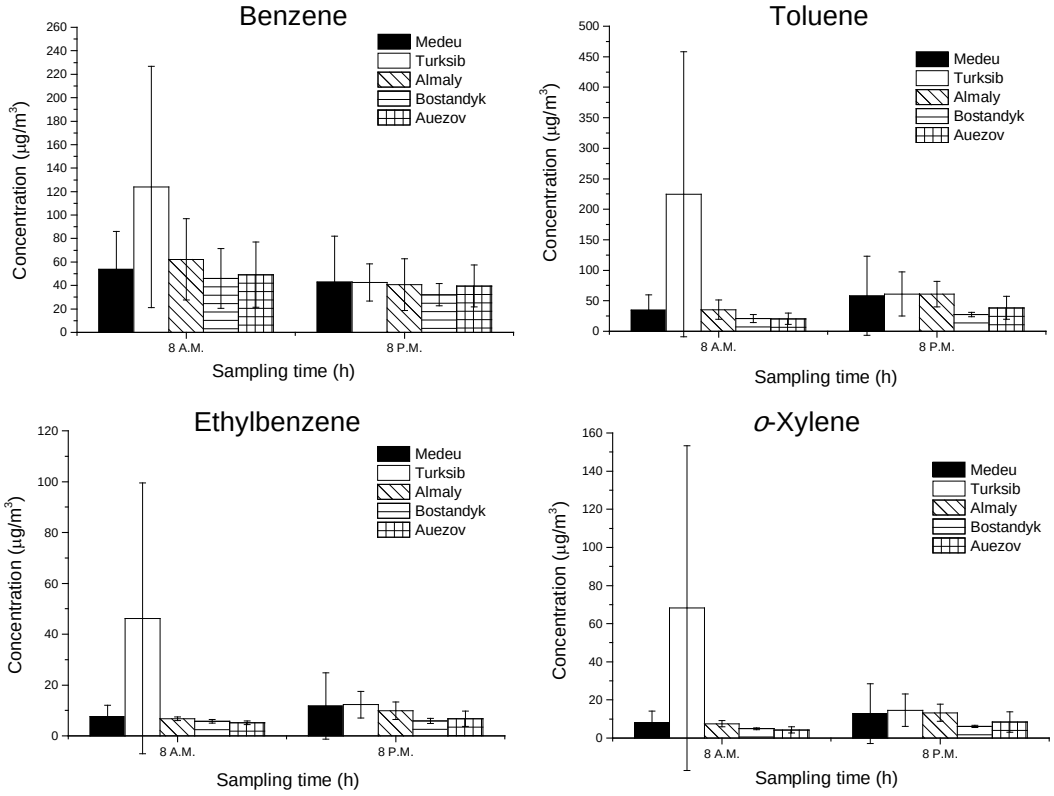

Figure 3 – BTEX concentrations in air of different districts of Almaty city

Daily mean BTEX concentrations (mean concentration for morning and evening sampling periods and six locations at a single day) ranged from 25 to 74 μg/m^3, 39 to 79 μg/m^3, 7 to 16 μg/m^3, and 8 to 22 μg/m^3, respectively (Fig. A5 in SM). The lowest BTEX concentrations were measured on Saturday (April, 4) likely due to higher temperature, improved air circulation in the Almaty airshed and lower traffic. In addition, higher day-night air temperature differentials encourage air exchange and speed up chemical reactions in the air.

BTEX concentrations are regulated all over the world (Table 1). Concentrations of BTEX in Almaty, Kazakhstan are close to reported concentrations of BTEX in cities with major air quality problems such as New Delhi, Cairo, Rome, Ho Chi Minh City, Sao Paulo, or Manila (Table 1) where vehicle exhausts are the main sources of BTEX, such as in Almaty (Balanay and Lungu, 2009; Carlsen et al., 2013). The main difference of Almaty from these cities is a climate requiring efficient heating system in October-April. In Almaty, substantial part of pollution (about 20%) originate from emission of power plants and private residential heating systems (Carlsen et al., 2013).

BTEX concentrations were inversely proportional to the altitude of the sampling sites (Fig. 4). In the upper, southern part of Almaty (closer to the mountains), concentrations of BTEX were slightly lower than those at the lower parts (Table A3 in SM, due to the absence of major industrial factories and wind direction from the mountains downward towards the city. The average elevation of the upper part of the city is 1,000 meters. At that altitude, there are more deciduous and coniferous trees and herbs, which may absorb hydrophobic BTEX (Kolmakov, 2015).

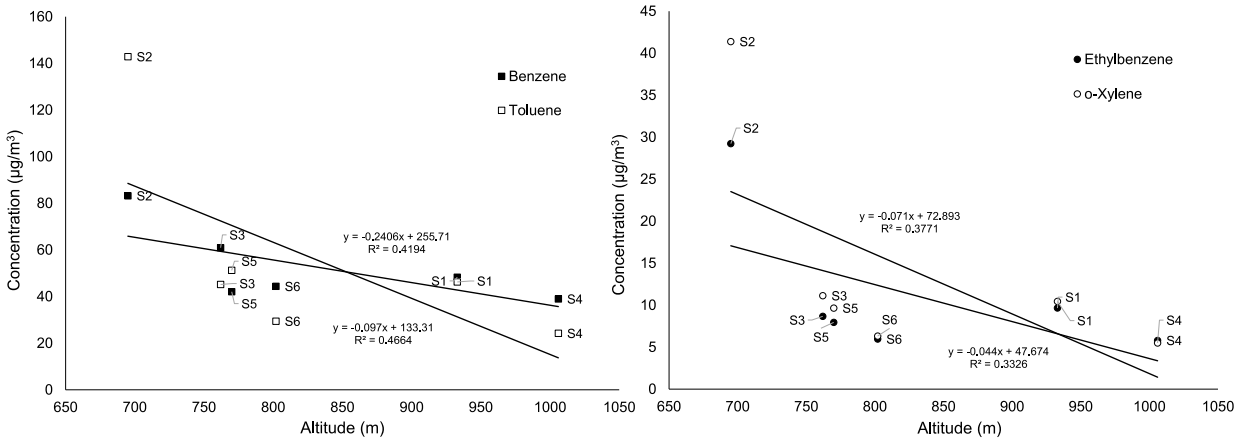

Figure 4 – Effect of altitude on measured BTEX concentrations

3.2 Statistical analyses of BTEX concentrations – effects of time of day, sampling day, and location

ANOVA studies were performed applying the R statistical software (R Core Team, 2015). There was no statistically significant difference between the single sampling sites. Thus, we focused on (1) daily variation between morning and evening samplings and (2) day-to-day variation mornings and evenings. Considering weather conditions for each sampling day, it is apparent that the three days are not identical. As shown in Table 2, sampling days were significantly different (Kazhydromet, 2015).

Hence, in the case of benzene we found statistical significance for concentration decreases from 8 A.M. to 8 P.M. for day 1 and day 2, whereas for day 3 virtually no change in the benzene concentration during the day was observed. For toluene, ethylbenzene and *o*-xylene, the median values were higher in the evening than in the morning. However, only for day 2 statistical significance was observed between morning and evening concentrations. For day 2, there was a snowfall in the morning and the occurrence of traffics jams was observed throughout the city. Thus, benzene concentrations were significantly lower at 8 P.M. than those at 8 A.M. (95% level, p=0.0013) (Fig. 5A), whereas concentrations of toluene (Fig. 5B), ethyl benzene (Fig. 5C) and *o*-xylene (Fig. 5D) were all higher in the evening (95%, p=0.015, 90%, p=0.070, and 95%, p=0.037, respectively). For day 3, benzene concentrations were lower in the evening (weak statistical significance at the 90% level, p=0.098). On day 1, it was sunny and later snowing overnight. Next sampling day, the weather became warmer, temperature of air from day 1 to day 3 varied from -10/-4 °C to +4/+11 °C (Table 2).

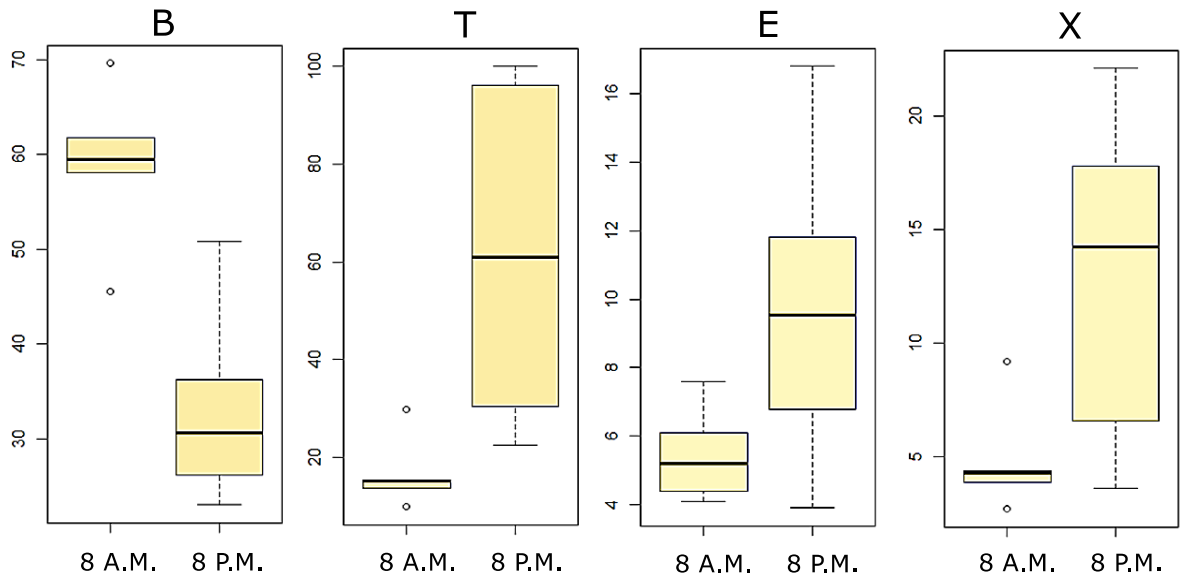

Figure 5 – Variation in concentrations of B: benzene, T: toluene, E: ethyl benzene and X: *o*-xylene between morning (8 A.M.) and evening (8 P.M.)

Day-to-day variations were significant. Thus, both for the 8 A.M. (Fig. 6A) and the 8 P.M. (Fig. 6B) samplings benzene concentrations were significantly decreasing from day 1 to day 2 (8 A.M.: 95% level, $p_{\text{day 1, day 2}}$= 0.046, 8 A.M.: 95% level $p_{\text{day 2, day 3}}$= 3.2e-4) and further to day 3 (8 P.M.: 95% level, $p_{\text{day 1, day 2}}$= 0.0046, 8 P.M.: 90% level $p_{\text{day 2, day 3}}$= 0.067). In the cases of toluene, ethyl benzene and *o*-xylene the 8 A.M. concentrations were found to drop from day 1 to day 2 and the increase again to days 3, whereas for the 8 P.M. samplings non-statistically significant decreases were observed from day 1 to day 2 and further to day 3. Further data will be necessary for more in-depth analyses, e.g., including variations from location to location, which based on the available data is not possible.

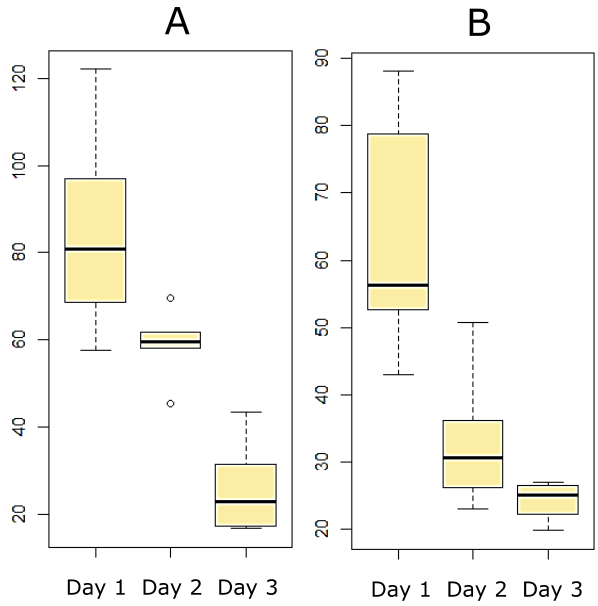

Figure 6 – Day-to-day variation of benzene. A: 8 A.M., B: 8 P.M.

3.3 Identification of BTEX emission sources

Toluene to benzene concentrations (T/B) ratio depends on the main source of air pollution, distance from the source and environmental conditions (Guo et al., 2007; Kerbachia et al., 2006; Khoder, 2007). The T/B ratio in the studied air samples increased with the increase of the air temperature (Figure 7). Five measurements provided T/B ratios higher than 2. The highest T/B ratio (3.4) was observed in Turksib district. At sub - 0 °C sampling temperatures, the T/B ratio was below 1 in 15 out of 18 samples. Such ratios may indicate that significant fraction of BTEX originate from non-traffic related sources (Liu et al., 2015; Moreira dos Santos et al., 2004). At lower temperatures, residential heating is likely the main source of BTEX. In Almaty, most power plants and private houses use natural gas and coal as fuel. On Saturday evening, in half of all sampling locations, the T/B ratio was close to 1. This may be due to the proximity of these locations to districts with private houses, where on Saturdays local people traditionally prepare their own

saunas for steaming and washing. In addition, the amount of traffic on the weekend is much lower compared to weekdays.

Thus, the bulk of BTEX emissions in Almaty originate both from traffic and residential heating. The obtained results indicate that at lower temperatures, more BTEX likely originate from heating while at higher temperatures – from traffic. These results are in agreement with our previous data indicating that end of heating season in Almaty correlated with decreased BTEX concentrations in ambient air by the factor of 3 to 5 (Bektasov et al., 2015). However, more research is required to confirm this finding.

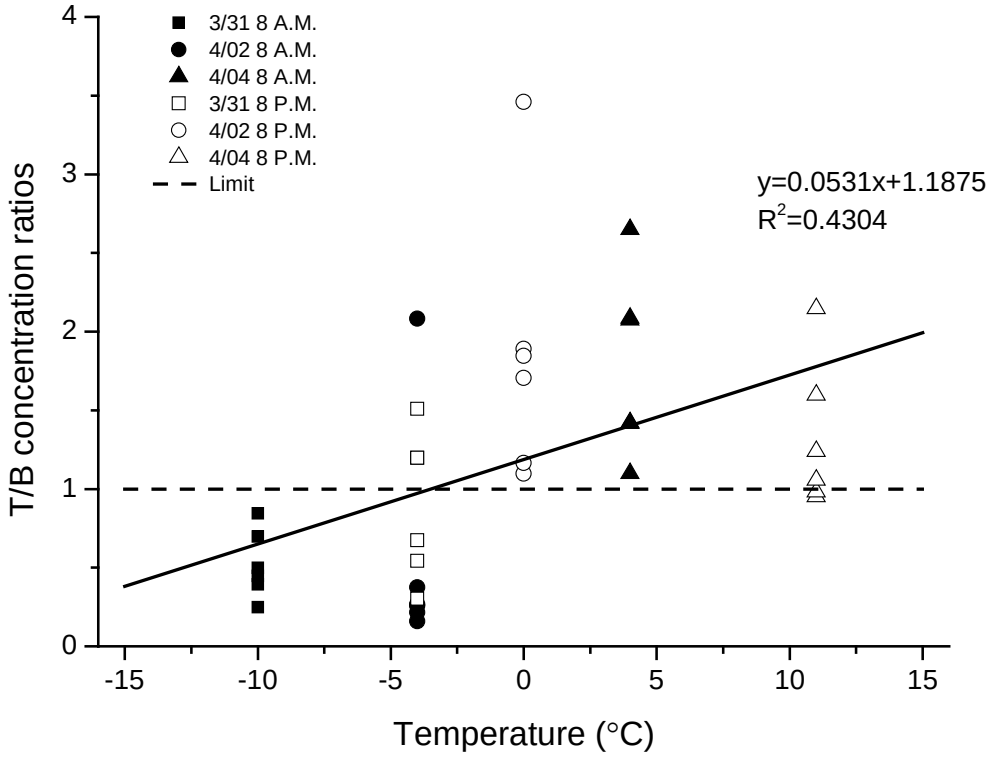

Figure 7 – Toluene/Benzene concentration ratios at different sampling sites and sampling days and times

Conclusion

The main results of this research are as follows:

– Simple whole air sampling method for BTEX was developed utilizing crimped vials, SPME and GC-MS. For quantification of BTEX, external standard methods was used; however slope factors of calibration plots were determined by a standard addition method, which did not require a “zero” air. Measurement errors were low considering the simplicity of collection method. New method can be a good alternative for low-budget air quality monitoring for BTEX. Adding new target VOCs of concern to urban air quality is possible with this method. The optimized

approach based on SPME-GC-MS appears as an attractive alternative for air pollutants monitoring in developing countries. Further improvement could require reducing the detection limit, which is possible by using a shorter GC column or more selective & sensitive detector, such as a triple quadrupole MS. It is also possible to increase the effectiveness of SPME fiber by using 20 mm fiber length.

– At different sampling times, mean concentrations of benzene, toluene, ethylbenzene and *o*-xylene in ambient air samples from Almaty, Kazakhstan ranged from 24 to 89, from 32 to 96, from 6 to 23 and from 7 to 32 μg/m^3, respectively. Lowest BTEX concentrations were determined on Saturday due to higher temperature and lower traffic. Mean BTEX analyte concentrations over all locations and sampling periods were 53, 57, 11 and 14 μg/m^3, respectively, being comparable with those in the most polluted cities around the world. Further research of greater scope and duration is warranted. Several aspects deserve more work, e.g., diurnal and seasonal variations, and addition of other primary air pollutants (e.g., PM-10, PM-2.5, SOx, NOx, CO, and ozone. Our earlier work (Carlsen et al., 2013) showed the presence of PAHs. Caution should be exercised when interpreting results that stem from this relatively short in duration air quality survey. More research that focuses on long-term (e.g., all seasons), weekday vs. weekend, and diurnal variations is warranted. Specific focus on the effects of elevation (and therefore location within the city), atmospheric inversions, wind direction, and levels of other important air pollutants such as PM, CO, SOx, NOx, ozone, and PAHs should be studied.

– Single BTEX concentrations in ambient air of Almaty were always below local regulatory thresholds. However, these thresholds are not very useful because: 1) they were established >15 y ago and have not been updated since then; 2) they are much higher than those for many other countries. The review and update of air quality standards is recommended considering ancillary public health reports from the region.

– ANOVA studies showed that measured benzene concentrations dropped significantly from the 8 A.M. sampling to the 8 P.M. sampling, whereas the reverse was observed for concentrations of toluene, ethylbenzene and xylene possibly due to lower vapor pressures and a high tendency to bind to a particular matter.

– A significant day-to-day variation was found. For both the 8 A.M. and the 8 P.M. samplings, benzene concentrations significantly dropped from day 1 to day 2 and further to day 3, whereas for toluene, ethyl benzene and o-xylene a concentrations were observed to decrease from day 1 to day 2 and then increase again on day 3. These variations are not immediately understandable but are assumed to be due to changing weather conditions in combination with BTEX vapor pressure differences and their affinity to bind to a particulate matter.

– The T/B ratios varied depending on a sampling temperature. At lower (below 0 °C) temperatures, T/B ratios were mostly below 1 meaning that significant fraction of BTEX originate from residential heating. At higher temperatures, the T/B ratios were mostly higher than 1 indicating that BTEX originate from traffic. More research over longer time periods is needed to confirm these findings.

It is recommended that coordinated research, regulations, and education work towards the decrease of BTEX concentrations and improving overall air quality in Almaty begins. There are many good examples of how elevated levels of air pollutants were lowered using civic involvement and multi-agency approach. More stringent car exhausts emission and fuel quality control, public awareness, education, and incentivizing technological and behavioral changes can work.

Supporting information

Additional information as noted in the text. This information is available free of charge.

Conflict of interest

The authors declare no competing financial interests.

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